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Kinetic Studies on Photodeposition of Polydiacetylene Thin Films from Solution: Preliminary Determination of the Rate Law

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Preliminary kinetic studies were undertaken on the photodeposition of thin films of a polydiacetylene derivative of 2-methyl-4-nitroaniline from monomer solutions onto quartz substrates. Solutions of the monomer, DAMNA, in 1,2-dichloroethane at various concentrations were irradiated at 364 nm using an argon-ion laser at several intensities. It was found that the rate of polydiacetylene (PDAMNA) film photodeposition varies linearly with UV light intensity and as the square root of monomer concentration.

Introduction

Recently we have reported on a novel surface photopolymerization reaction in which polydiacetylene thin films are deposited from diacetylene monomer solutions onto transparent substrates upon irradiation with UV light.^{1,2} Specifically, we discovered that amorphous films of a polydiacetylene derivative of 2-methyl-4-nitroaniline (PDAMNA) are formed readily when solutions of the monomer (DAMNA) in solvents such as 1,2-dichloroethane are irradiated with long-wavelength UV light through glass or quartz windows, which serve as the substrate. This simple, straightforward process yields transparent yellow-orange PDAMNA films with thicknesses on the order of a micrometer. Because this reaction is newly discovered, there is a considerable amount of fundamental science to be learned about the kinetics, photochemistry, surface chemistry, and mechanism of the process. In this article the results of some preliminary kinetic studies on the photodeposition of PDAMNA films from solution are described.

We start by assuming that the rate law for polydiacetylene film photodeposition can be given by a single expression of the form

$$dl/dt = kI^m C^n \quad (1)$$

where l is film thickness, t is time, I is the intensity of the UV radiation (at the surface of the growing film), C is monomer concentration, m and n are the orders of the reaction in radiation intensity and monomer concentration, respectively, and k is the rate constant.

Applying the Beer-Lambert law of absorption of radiation to the film,³ we have

$$I = I_0 e^{-\epsilon l} \quad (2)$$

where I_0 is the intensity of the UV source (before entering the film), I is the intensity after traveling

distance l through the film (i.e., at the surface of the film in contact with the monomer solution where photodeposition is occurring), and ϵ is the absorption coefficient of the film.

Under conditions of constant UV source intensity and constant monomer concentration during the reaction (pseudo-zeroth-order kinetics), and making use of eq 2, eq 1 can be integrated to give

$$l = (1/m\epsilon) \ln(m\epsilon k I_0^m C^n t + 1) \quad (3)$$

Since the absorbance of the film, a , is given by $a = \epsilon l$, this equation can be rearranged to give

$$a = (1/m) \ln(m\epsilon k I_0^m C^n t + 1) \quad (4)$$

Hence, if we carry out polydiacetylene film photodeposition under pseudo-zeroth-order conditions, i.e., use an excess of monomer, follow only the early portion of the reaction so that monomer concentration remains essentially constant, and maintain constant UV source intensity, the kinetics of the reaction should follow eq 4. Therefore our experimental method consists of measuring the absorbance of the film at various time intervals for several monomer concentrations and UV source intensities, fitting the data to eq 4, and determining the order parameters m and n and the rate constant k .

Methods and Results

Because photodeposition of PDAMNA films occurs best at long wavelengths, the 364 nm radiation from an argon-ion laser was chosen as the UV source; the use of a laser ensures that the radiation is monochromatic and allows better control and determination of the radiation intensity. To verify that the PDAMNA films follow the Beer-Lambert law, UV-visible spectra were obtained on four films with varying thicknesses. A plot of the absorbance at 364 nm versus thickness for each film results in a good straight line (Figure 1), thus confirming that the Beer-Lambert law is indeed obeyed.

It was decided to first do a series of runs in which only the intensity of the UV source is varied in order to determine the order of photodeposition in UV intensity,

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(1) Paley, M. S.; Frazier, D. O.; Abdeldeyem, H.; McManus, S. P. *Chem. Mater.* 1994, 6, 2213.

(2) Paley, M. S.; Frazier, D. O.; Abdeldeyem, H.; Armstrong, S.; McManus, S. P. *J. Am. Chem. Soc.* 1995, 117, 4775.

(3) *Physical Chemistry*, 3rd ed.; Atkins, P. W., W. H., Ed.; Freeman and Company: New York, 1986; p 464.

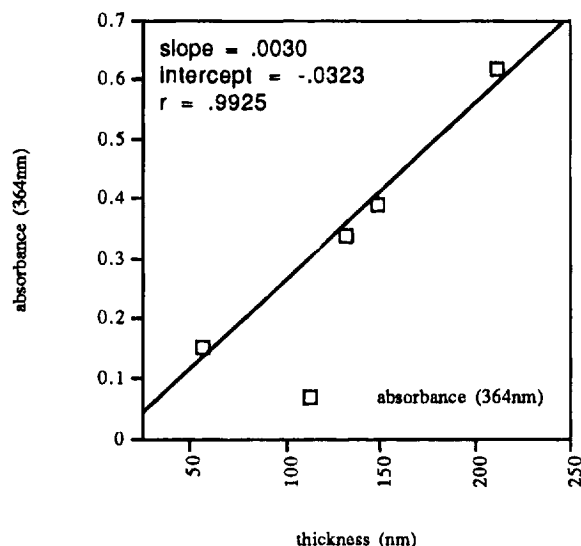


Figure 1. Absorbance versus thickness data for PDAMNA films.

Table 1. Absorbance of PDAMNA Films at 364 nm (Monomer Concentration 2.5 mg/mL)

intensity (mW/cm ²)	time (min)			
	30	60	90	120
1.6	0.0821	0.1458	0.1882	0.2351
3.2	0.1368	0.2121	0.3094	0.3888
6.4	0.1992	0.3833	0.4893	0.6023
9.5	0.2946	0.4703	0.6494	

i.e., to determine the value of the parameter m . Thus a series of runs were carried out, each at a DAMNA monomer concentration of 2.5 mg/ml (0.01 moles/liter) in 1,2-dichloroethane, with varying UV source intensities. The data are summarized in Table 1.

Since the monomer concentration, C , remains constant throughout all of these runs, the quantity C^n also remains constant and therefore so does the entire quantity $m\epsilon kC^n$ in eq 4. Thus for simplicity we can define a new constant $K = m\epsilon kC^n$ and rewrite eq 4 as

$$a = (1/m)\ln(KI_0^m t + 1) \quad (5)$$

To determine the values of the parameters m and K , the data from Table 1 are curve fitted to eq 5. Because the equation is nonlinear, the Levenburg–Marquardt^{4,5} method was chosen to fit the data. This yielded values of $m = 0.84$ and $K = 1.2 \times 10^{-3}$, with a correlation coefficient of 0.997. The results are shown graphically in Figure 2.

Because of minor fluctuations in the laser power and the variation in radiation intensity across the beam diameter (due to the Gaussian nature of the beam), we estimate that there is approximately a 10–15% uncertainty in our measurement of the UV radiation intensity. There is also about a 10% inherent error in the absorbance values because of small variations in film thickness and the difficulty of ensuring that the same spot on the film is measured each time. Comparisons with rate laws for other polymerization reactions, as

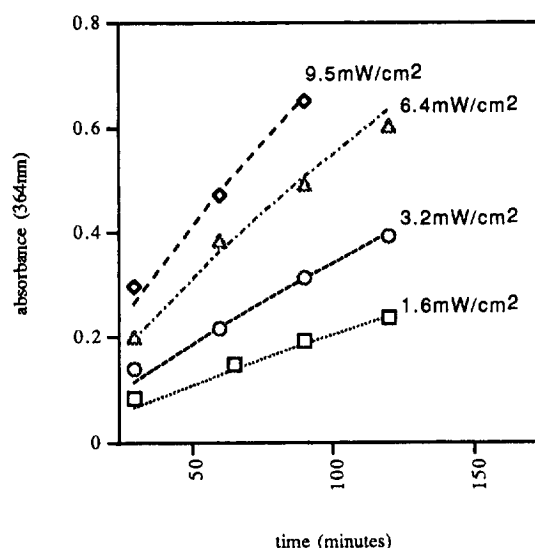


Figure 2. Curve fit of kinetic data from Table 1 to eq 5.

Table 2. Linear Regression Fit of Data from Table 1 to Eq 6

intensity (mW/cm ²)	slope	intercept	corr coeff
1.6	0.0020	1.027	1.000
3.3	0.0037	1.028	0.998
6.4	0.0066	1.041	0.997
9.5	0.0095	1.048	0.998

well as chemical intuition, leads us to expect that the parameters m and n should probably be integral or half-integral; i.e., they should have values of 0.5, 1.0, 1.5, 2.0, etc. On the basis of this and the inherent uncertainty in our experimental technique, we feel that the value of 0.84 for m should be rounded up to 1.0.

To see how well the data fits if we set $m = 1$, we can rearrange eq 5, with $m = 1$, as follows:

$$e^a = KI_0 t + 1 \quad (6)$$

Hence a plot of e^a versus t at fixed intensity should give a straight line with a slope of KI_0 and an intercept of unity. When the data from Table 1 are fitted using linear regression to eq 6, good straight lines are indeed obtained. The results are shown in Table 2.

In accordance with eq 6, if we plot the slope of each line versus intensity, the result should be a straight line with slope K and intercept zero. As seen from Figure 3, this is indeed the case; the intercept of 5×10^{-4} , when compared to the spread of the data (2.0×10^{-3} – 9.5×10^{-3}), is off from zero by only 7%. Thus, taking into account the inherent error of our experimental technique, we feel that it is reasonable to conclude that $m = 1$, which means that the rate of photodeposition depends linearly on UV radiation intensity.

Having determined the order of the reaction in light intensity, m , the next step is to determine the order in monomer concentration, n . This is accomplished in a similar fashion, only this time keeping the source intensity constant and varying the monomer concentration. Thus a series of runs were conducted, all under the same constant UV source intensity, at several different concentrations. The results are shown in Table 3.

Analogous to the previous case, since the source intensity I_0 remains constant, the entire quantity $m\epsilon kI_0^m$ remains constant. Also $m = 1$, and so eq 4 can

(4) *Nonlinear Parameter Estimation (An Integrated System in Basic)*; Nash, J. C., Walker-Smith, M., Eds.; Marcel Dekker Inc.: New York, 1987.

(5) *PSI-Plot, Technical Plotting and Data Processing, User's Handbook*; Poly Software International Ltd.: Salt Lake City, UT, 1992–1993; p 161–2.

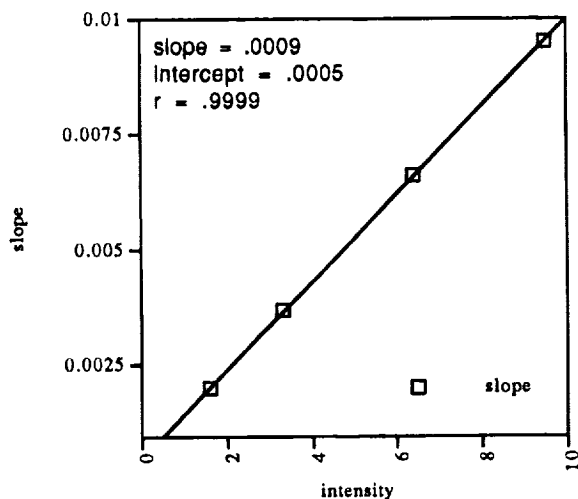


Figure 3. Slope versus intensity data from Table 2.

Table 3. Absorbance of PDAMNA Films at 364 nm (Constant UV Source Intensity)

concn (mg/mL)	time (min)			
	30	60	90	120
0.50	0.565	0.1030	0.1342	
0.83	0.0797	0.1408	0.1724	0.2085
1.25	0.0940	0.1563	0.1984	0.2576
2.50	0.1218	0.1808	0.2640	0.3352
3.50	0.1381	0.2072	0.3016	0.3734

Table 4. Linear Regression Fit of Data from Table 3 to Eq 7

concentration (mg/mL)	slope	intercept	corr coeff
0.50	0.0013	1.017	0.996
0.83	0.0016	1.042	0.991
1.25	0.0021	1.036	0.997
2.50	0.0030	1.030	0.996
3.50	0.0035	1.036	0.997

be rewritten as

$$e^a = K'C^n t + 1 \quad (7)$$

where $K' = m\epsilon k I_0$.

Hence a plot of e^a versus t at fixed concentration should give a straight line with a slope of $K'C^n$ and an intercept of unity. When the data from Table 3 are fitted to eq 7 using linear regression, good straight lines are obtained (Table 4).

In accordance with eq 7, the slope of each line is equal to $K'C^n$. Thus if we plot $\ln(\text{slope})$ versus $\ln(\text{concentration})$, the result should be a straight line with slope n . As seen from Figure 4, this is indeed the case, and a value of $n = 0.52$ results. Again, taking into account inherent experimental error, this value should be rounded down to 0.5. Thus the rate of photodeposition of PDAMNA from solution varies as the square root of concentration.

The last quantity to be determined is the rate constant k ; which can readily be obtained using the value of $K = 9.46 \times 10^{-4}$ from Figure 3. Recall that $K = m\epsilon k C^n$; since we know that $m = 1$ and $n = 0.5$, and, from Figure 1, we have that $\epsilon = 3.0 \times 10^{-3} \text{ nm}^{-1} = 3.0 \times 10^4 \text{ cm}^{-1}$, and last, from Table 1, we have $C = 2.5 \text{ mg/mL} = 0.01 \text{ mol/L}$, we can then determine that $k = 3.2 \times 10^{-7}$ (omitting units). To be clear, this is the value of k at ambient temperature (25 °C) when thickness is

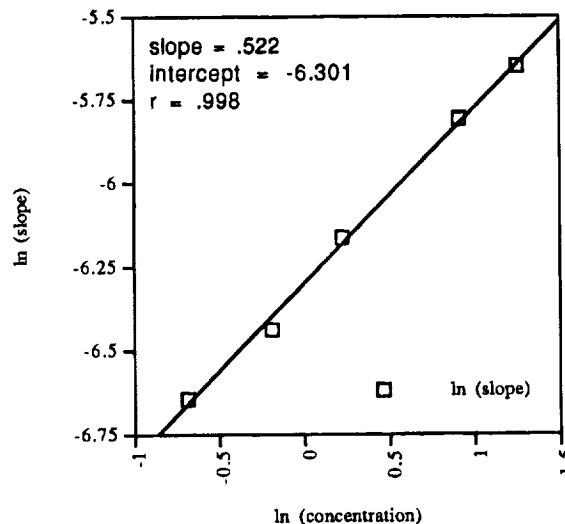


Figure 4. Slope versus concentration data from Table 4.

measured in centimeters, light intensity in mW/cm^2 , monomer concentration in mol/L , and time in seconds.

Conclusions

While the polymerization of diacetylenes has been studied somewhat in the solid state,^{6,7} virtually nothing has been reported in the literature on solution-state polymerization or on photodeposition of polydiacetylene films from solution. It may well be the case that the basic mechanism is essentially the same in all cases; however, this remains to be determined. We do know that triplet states are involved both in the solid state and in solution.² On the basis of our preliminary kinetic studies, it appears that the rate of photodeposition of PDAMNA films from solution is linear in UV light intensity (364 nm) and square root in monomer concentration. The one-half order in monomer concentration is very intriguing, it implies that the mechanism is not a simple process, whereby monomers collide with the surface and attach to form the polymer film. If such were the case one would expect the rate to be first-order in concentration. It is known that for solid-state polymerization of diacetylenes the mechanism involves biradical dimers and not monomers as the active precursors to polymerization.^{6,7} Possibly similar species are involved in solution. However, at this point, it would be premature to make conclusions about the mechanism of the reaction based only on this one rate law.

It is important to recognize that, so far, we have studied only the rate of polymer film deposition (a heterogeneous reaction) and not bulk solution polymerization (a homogeneous reaction). To really gain insight into the mechanism of diacetylene photopolymerization in solution, the rate law for bulk solution polymerization must also be determined. Followup studies are underway to verify our initial results and to study polymerization in the bulk solution. Also, future experiments are planned to determine the effects of triplet sensitizers and quenchers on the rate, as well as the effects of different solvents, substrates, UV wavelengths, and perhaps other variables. Hopefully

(6) *Polydiacetylenes*; Bloor, D., Chance, R. R., Eds.; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, 1985; pp 25–40.

(7) Sixl, H. *Adv. Polym. Sci.* **1984**, 63, 49.

these studies will allow us to gain greater insight into the mechanism of this novel and intriguing reaction.

Experimental Section

The synthesis and purification of DAMNA have been described previously.⁸ All solutions of DAMNA in 1,2-dichloroethane were filtered before use. As stated previously, the UV radiation (364 nm) from an argon-ion laser was used to grow the films. An attenuator was used to maintain constant light intensity during the kinetic runs. Light intensity was measured using United Detector Technology Model UDT-21A. The beam was opened to a diameter of 2 cm in order to grow films onto 1.5 cm diameter quartz substrate disks. Film thicknesses were measured using an Gaertner LC112 ellipsometer. UV-visible spectra were obtained on an HP8452 photodiode array spectrometer, using a blank quartz disk as a reference. Absorbance (364 nm) vs thickness data are shown in Figure 1.

(8) Paley, M. S.; Frazier, D. O.; McManus, S. P.; Zutaut, S. E.; Sangahdasa, M. *Chem. Mater.* **1993**, *5*, 1641.

Kinetic runs were carried out by filling the growth cell² with monomer solution, irradiating for 30 min at ambient temperature (25 °C), removing the quartz substrate, washing the PDAMNA film with 1,2-dichloroethane, and obtaining the UV-visible spectrum of the film. The film was then placed back in the growth cell, and the above sequence of steps was repeated to obtain the next data point in the run. Light intensity was determined before the start of each run, and during each 30 min break when the film was removed. Runs were carried out for a series of monomer concentrations and light intensities; the data are shown in Tables 1 and 3.

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